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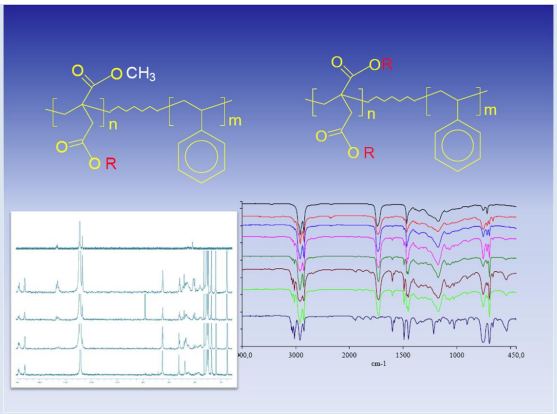
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COPOLYMERIZATIONS OF LONG SIDE CHAIN DI *N*-ALKYL ITACONATES AND METHYL N-ALKYL ITACONATES WITH STYRENE: DETERMINATION OF MONOMERS REACTIVITY RATIOS BY NMR

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ABSTRACT

Low yields copolymerization of styrene (S) with di-n-alkylitaconates (DI-n) and methyl n-alkylitaconates (MeI-n) with alkyl side chain of 12, 14, 16, 18 and 22 carbon atoms were carried out in bulk via radical at 60ºC with AIBN as initiator. The copolymers chemical structure was characterized by FTIR and 1H and 13C-NMR, and the composition was determined by 1H-NMR. The NMR studies indicate that the copolymers are random, but with some tendency to alternation. The monomers reactivity ratios between the styrene and itaconates in the copolymerization (ri) were calculated by the Fineman-Ross (FR), Kelen Tüdös (KT) methods and a modification of the last one. The obtained values of r1(DI) and r2(S) in the copolymerization among DI-n with n = 12, 14 and 16 with S were in the range of 0.22 to 0.28 for DI-n and 0.19 to 0.39 for S. Whereas for DI-n with n = 18 and 22 the values are in the order of 0.42-0.50 and 0.37-0.47 respectively. For the copolymer series derivatives of MeI-n the values were between 0.01-0.41 for the itaconate and 0.44-0.97 for S.

Keywords: *n-alkylitaconate, styrene, copolymerization, reactivity ratios*

COPOLIMERIZACIÓN DE DIITACONATOS Y METIL ITACONATOS DE N-ALQUILO DE CADENAS LATERALES LARGAS CON ESTIRENO: DETERMINACIÓN DE DE LAS RELACIONES DE REACTIVIDAD DE LOS MONÓMEROS POR RMN.

RESUMEN

La copolimerización a bajos grados de conversión de estireno (S) con di-n-alquilitaconatos (DI-n) y de metil-n-alquil itaconatos (MeI-n) con cadenas laterales de 12, 14, 16, 18 y 22 átomos de carbono se llevó a cabo por vía radical, en masa a 60ºC y empleando AIBN como iniciador. La estructura química de los copolímeros se caracterizó por FTIR y RMN-1H y 13C y la composición se determinó por RMN-1H. Los estudios de RMN indican que los copolímeros son estadísticos pero con cierta tendencia a la alternancia. Las relaciones de reactividad (ri) entre el estireno e itaconatos se calcularon mediante los métodos de Fineman-Ross (FR), Kelen Tüdös (KT) y una modificación esta última. Los valores obtenidos de r1(DI) y r2(S) en la copolimerización entre los DI-n con n = 12, 14 y 16 con S estuvieron en el rango de 0.22 a 0.28 para DI-n y 0.19 a 0.39 para S, mientras que los valores encontrados para los DI-n con n = 18 y 22 son del orden de 0.42-0.50 y 0.37-0.47 para el itaconato y estireno respectivamente. Para la serie de MeI-n, los valores oscilaron entre 0.01 hasta 0.41 para los itaconatos y 0.44 a 0.97 para el S.

Palabras Claves: *n-alquilitaconatos, estireno, copolimerización, relaciones de reactividad*

1. INTRODUCTION

Polyitaconates have been widely studied for decades possibly due to its structural similarity with the polyacrylates and polymethacrylates and by the low cost of the itaconic acid, substance from which the itaconates are obtained [1]. Many of these researches have been oriented to the study of the amorphous state and properties in dissolution [1-4], while others have focused in the study of their thermal degradation [5-9]. A more recent studies carried out with a series of poly(mono *n*-alkyl itaconate)s, poly(methyl *n*-alkyl itaconate)s and poly(di-*n*-alkyl itaconate)s with n = 12, 14, 16, 18 and 22 showed that from certain size, the *n*-alkyl side-chains are able to crystallize [10, 11].

The copolymerization of itaconates with vinyl monomers had also received some attention, for example, the copolymerization of methyl and butyl diitaconates with vinyl monomers as styrene and methyl methacrylate had been studied [12-19]. On the other hand, a long side chain series of mono *n*-alkyl itaconates [20] and the *n*-hexadecyl diitaconate [21] were copolymerized with styrene. For these copolymers the *n*-alkyl side chains were able to crystallize depending on both the copolymer composition and their length. Even though, there have been a considerable number of studies on the copolymerization of itaconate with vinyl monomers, only very few of them report on the reactivity ratios between monomers. So for example, the reactivity ratios in the copolymerization of styrene with mono *n*-alkyl itaconates with n = 6-12 [22, 23] and 1-menthyl itaconate derivatives [24, 25] were described. The possibility of copolymerized itaconates with vinyl monomers would improve the properties of these materials and the formation of gels would also enhance the application of these materials making them good candidates to be used in the manufacture of purification devices such as filters and membranes or as filler for analytical columns [26].

Since the little knowledge about the reactivity ratios of the copolymetization between styrene and *n*-alkyl itaconates, the possible influence of proportion and how the monomers are distributed in the copolymer chain on the final properties of the copolymers, in the present work we propose to carry out a NMR study with the main aim of determining the values of reactivity ratios in the copolymerization of styrene with a series of di *n*-alkyl and methyl *n*-alkyl itaconates containing an even number of carbon atoms from 12 up to 22 in the alkyl chain. They were copolymerized at low conversions (<10%) and the reactivity ratios were determined using the Finemann-Ross and Kelen-Tüdös methods [27, 28]. A new treatment which involves the modification of some Kelen-Tüdös parameters was also tried and the results were compared with those obtained by Finemann-Ross and Kelen-Tüdös methods, which are widely used in the determination of the reactivity ratios for great quantity of systems.

2. EXPERIMENTAL PART

2.1 Materials

Styrene (99.9 %) was dried over CaH_2 and distilled under reduced pressure.

Itaconic acid (Aldrich 99.9 + %) and other chemicals (analytical grade or better) were used without further purification.

2.2 Monomer synthesis

Di-*n*-alkyl-itaconates (DI-*n*) were synthesized by esterification of itaconic acid with the corresponding alcohol using *p*-toluenesulfonic acid as catalyst. MeI-*n* were synthetized by methylation of the corresponding mono-*n*-alkyl-itaconates (MI-*n*) with diazomethane following methods previously reported [10, 11].

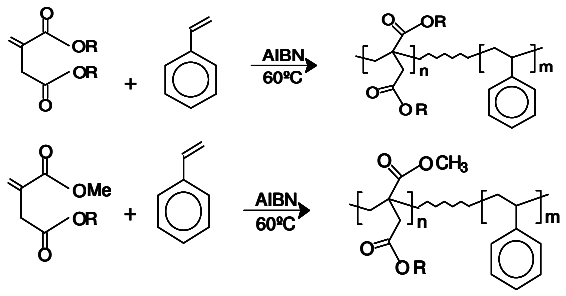
MI-*n* were prepared essentially in the same way described for DI-*n* using acetyl chloride instead of *p*-toluenesulfonic acid as catalyst [10, 11].

2.3 Polymerization

Polymerizations of both series were carried out in bulk at 60ºC under nitrogen atmosphere using AIBN (1% molar) during 1 hour, the time required to reach about 5-10% yields. The molar ratio itaconate/styrene in the feed was varied between 4:1 and 1:4. The obtained copolymers were purified by dissolving in chloroform and precipitating with methanol. The purification method was repeated several times. In some cases it was necessary to boil the copolymers with methanol to eliminate the unreacted itaconate. Yields were determined gravimetrically based on the weight of the starting monomers. The nomenclature used for these copolymers is DI-*n*-*co*-S and MeI-*n*-*co*-S (X:Y) where *n* is the carbon number of the itaconate side chain and X represents the molar proportion of the itaconate and Y of styrene used in the feed.

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In the Figure 1 is shown a scheme of the copolymerization reaction between the diitaconates and methyl itaconates with styrene.



R: $C_{12}H_{25} - C_{22}H_{45}$

Figure 1. Copolymerization reactions between the itaconates and styrene.

2.4 Characterization

Infrared spectra were registered on a Fourier Transform Infrared Spectrophotometer (FTIR) Perkin-Elmer System 2000. The samples were prepared on NaCl discs by casting from $CHCl_3$ solutions.

NMR spectra were recorded on a Bruker AVANCE DRX 400 spectrometer at room temperature from samples dissolved in $CDCl_3$ using tetramethylsilane (TMS) as internal reference.

2.5 Reactivity ratios determination

Reactivity ratios between DI and MeI with styrene in the copolymerization were determined using both the Fineman-Ross (FR) [13] and the Kelen Tüdös (KT) [14] methods. Furthermore, a third new strategy is used for the first time in this paper. The Fineman-Ross equation is:

$$\frac{f(F-1)}{F} = \left(\frac{f^2}{F}\right) r_1 - r_2 \qquad (1)$$

Where, f is the molar ratio of the monomers in the feed and F in the copolymer. Then from the representation of $f(F-1)/F$ vs f^2/F it can be obtained r_1 and r_2 from the slope and the origin.

The Kelen Tüdös equation introduces an arbitrary constant α with the aim to separate the data uniformly and at the same time allows that all the points have the same statistical weigh, and is expressed as:

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha} \qquad (2)$$

Where: $\eta = G/(\alpha + H)$, $\alpha = \sqrt{H_{mín.}.H_{máx.}}$, $\xi = H/(\alpha + H)$, $G = f(F-1)/F$, $H = f^2/F$. As in the former case if is plotted η vs. ξ the values of r_1 y r_2 can be obtained from the origin and the slope.

A modification of the KT equation was also used for the determination of the reactivity ratios and was realized by a rearrangement of the copolymer composition equation:

$$F_1 = \frac{r_1 f_1^{\,2} + f_1 f_2}{r_1 f_1^{\,2} + 2 f_1 f_2 + r_2 f_2^{\,2}} \qquad (3)$$

to obtain a new expression where r_1 and r_2 have the same weigh in the equation:

$$(F_1 - F_2) = \frac{f_1}{f_2} F_2 r_1 - \frac{f_2}{f_1} F_1 r_2 \qquad (4)$$

Then we define:

$$(F_1 - F_2) = \beta(r_2 + r_1) + \delta(r_2 - r_1) \qquad (5)$$

Where, β and δ are two arbitrary constants.

Equaling (4) to (5) we obtain,

$$\beta = 1/2(f_1/f_2)F_2 - 1/2(f_2/f_1)F_1 \quad \text{and}$$

$$\delta = -1/2(f_1/f_2)F_2 - 1/2(f_2/f_1)F_1 \qquad (6)$$

If equation (5) is used and $(F_1 - F_2)$ is plotted vs. β, the slope value is $(r_2 + r_1)$ and the origin will be $\delta(r_2 - r_1)$.

Due to the sensibility of r_1 and r_2 to the mathematical manipulation, the new methodology proposed here, in conjunction with the most classical treatments of FR and KT, provides an additional verification and a statistical support for the values of reactivity ratios reported. The equation works very well as long as the origin $\delta(r_2 - r_1)$ is small.

3. RESULTS AND DISCUSSION

3.1 Copolymer characterization and compositions determination

Using the reaction conditions described above, both series of copolymers were obtained free of monomer

with yields of about 10% or less. In Tables 1 and 2 are shown the composition of the monomers in the feed and in the copolymer as well as their yields.

The physical appearance of copolymers varies depending on the composition and the length of the side chain of the itaconate units. Then, copolymers constituted by any of the itaconates with 12, 14 or 16 carbon atoms in the side chain and a small quantity of S, were sticky and transparent, but when the amount of S is increased the copolymers become white and gummy. On the other hand, those copolymers composed by itaconates of 18 or 22 carbon atoms in the side chain are white powders and become more rigid as the amount of styrene increase.

FTIR spectra of all of copolymers were similar and exhibit the characteristic bands of both moieties. In Figure 2 are shown as example, the spectra of the series of DI*18*-*co*-S compared with the Poly(di-*n*-octadecyl itaconate) (PDI-*18*) and polystyrene (PS).

There it can be seen qualitatively that the most important bands of the styrene moiety, in the region 3100-3000 cm-1 (stretching =C-H of the aromatic ring), 1602 cm-1 (symmetric ring stretch), 1500 cm-1 (ring stretch), 1450 cm-1 ("sideways" ring stretch) and 760 and 700 cm-1 (symmetric and no symmetric out-of-plane ring bending), diminish their intensities in comparison with those of the itaconate, as the itaconate ratio increases.

Table 1. Monomers molar ratios in the feed, composition of the DI-*n*-*co*-S copolymers and yields obtained in the copolymerization.

f_1/f_2 (I/S)[a]	F_1/F_2 (I/S)[b]	Yield (%)	F_1/F_2 (I/S)[b]	Yield (%)	F_1/F_2 (I/S)[b]	Yield (%)	F_1/F_2 (I/S)[b]	Yield (%)	F_1/F_2 (I/S)[b]	Yield (%)
	DI-*12*-*co*-S		DI-*14*-*co*-S		DI-*16*-*co*-S		DI-*18*-*co*-S		DI-*22*-*co*-S	
4:1	0.63/0.37	8.4	0.62/0.38	8.4	0.67/0.33	3.4	0.72/0.28	9.4	0.73/0.27	7.9
3:1	0.62/0.38	7.5	0.59/0.41	7.5	0.58/0.42	4.6	0.71/0.29	8.7	0.66/0.34	6.7
2:1	0.61/0.39	6.4	0.57/0.43	6.4	0.56/0.44	6.7	0.60/0.40	6.9	0.61/0.39	9.3
1:1	0.47/0.53	9.0	0.56/0.44	3.0	0.47/0.53	5.5	0.48/0.52	9.8	0.47/0.53	8.6
1:2	0.39/0.61	10.1	0.43/0.57	5.0	0.43/0.57	3.0	0.39/0.61	8.0	0.41/0.59	7.7
1:3	0.34/0.66	8.6	0.36/0.64	9.5	0.37/0.63	6.5	0.33/0.67	10.0	0.38/0.62	10.2
1:4	0.29/0.71	9.5	0.31/0.69	7.2	0.30/0.70	7.6	0.29/0.71	10.1	0.29/0.71	9.1

I: Itaconate, S: Styrene. [a] f_1/f_2 (I/S): Molar fraction of the monomers in the feed. [b] F_1/F_2 (I/S): Copolymers composition measured by ^{1}H-NMR (expressed in molar ratios).

Table 2. Monomers molar ratios in the feed, composition of the MeI-*n*-*co*-S copolymers and yields obtained in the copolymerization.

f_1/f_2 (I/S)[a]	F_1/F_2 (I/S)[b]	Yield (%)	F_1/F_2 (I/S)[b]	Yield (%)	F_1/F_2 (I/S)[b]	Yield (%)	F_1/F_2 (I/S)[b]	Yield (%)
	MeI-*12*-*co*-S		MeI-*14*-*co*-S		MeI-*16*-*co*-S		MeI-*18*-*co*-S	
4:1	0.47/0.53	5.4	0.57/0.43	5.6	-	-	0.63/0.37	6.6
3:1	-	-	0.50/0.50	8.2	0.61/0.39	6.9	0.62/0.38	7.8
2:1	0.41/0.59	6.2	-	-	0.59/0.41	7.8	0.60/0.39	8.5
1:1	-	-	0.44/0.56	7.5	-	-	0.47/0.53	6.5
1:2	0.26/0.74	4.0	0.34/0.66	4.6	0.28/0.72	8.0	-	-
1:3	-	-	0.28/0.72	5.9	0.23/0.77	8.5	0.34/0.66	8.9
1:4	-	-	0.24/0.76	8.2	0.21/0.79	5.4	0.29/0.71	7.7

I: Itaconate, S: Styrene. [a] f_1/f_2 (I/S): Molar fraction of the monomers in the feed. [b] F_1/F_2 (I/S): Copolymers composition measured by ^{1}H-NMR (expressed in molar ratios).

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The NMR spectra obtained from the series of DI-n-co-S or MeI-n-co-S were similar to each other, and like the FTIR spectra, the intensity of the signals of itaconate and styrene changes as the composition does. Figure 3 shows the 1H-NMR spectra of MeI-18 (A) and MeI-18-co-S (1:1) (B) with the respective assignations. In the figure it can be appreciated the spectrum of DI-18-co-S (1:1) (C) for comparison. The signal assignations were confirmed by bidimentional NMR techniques [29].

The composition of the copolymers reported in Table 1 was determined by ^{1}H-NMR, comparing the integral of the signals of the $-CH_3$ at 0.9 ppm of the side chains of the itaconate (e for MeI-*18*-*co*-S and e and e´, for DI-*18*-*co*-S) with the aromatic protons of the styrene (*o*, *m*, *p*) (6.30-7.25 ppm). The absence in the copolymers spectra of the two signals between 5.7 and 6.4 ppm and the triplet at approximately 4.2 ppm corresponding to the $=CH_2$ protons and to the OCH_2 of the side chain of the monomer also indicate that the copolymers were free of monomers. On the other hand, in the spectrum of the MeI-*18*-*co*-S (Figure 3B) it may be observed that the signal of OCH_3 and the OCH_2, (b´) and (b) respectively, are not only shifted in comparison with the corresponding signal of the homopolymer (Figure 3A) [10, 11] but also are highly split in broad signals. This was also observed, although with less intensity for DI-*18*-*co*-S (Figure 3C). This fact not only indicates that the copolymerization was successfully carried out, but also suggests that the units of styrene and itaconate are randomly distributed in the copolymer chain.

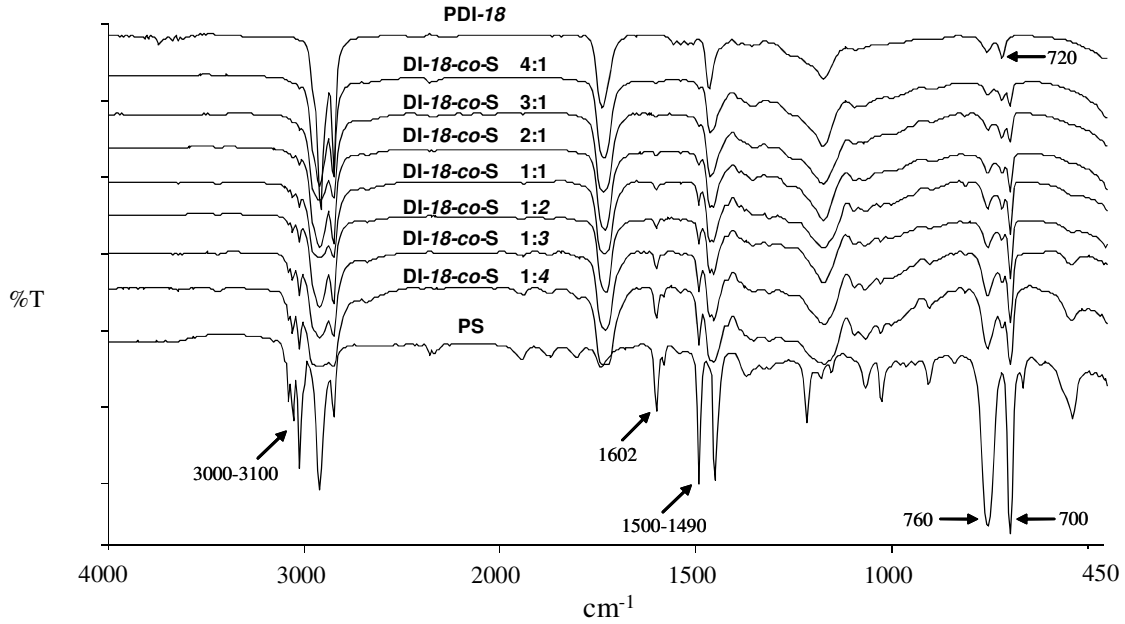


Figure 2. FTIR spectra of the series of DI-*18*-*co*-S copolymers compared with both homopolymers. Arrows indicate the bands where are observed the most notable changes (see text).

The ^{13}C-NMR studies confirm the results described above. In Figure 4 The DEPT 135 spectrum of MeI-*18*-*co*-S(1:1), which is considered representative of all the series, is compared with polystyrene, and PMeI-*18* spectra.

In the copolymer spectrum the signals of the carbons directly attached to the carbonyl groups (OCH_3 and OCH_2) of the itaconate units (a and e) are split in several signals and shifted to higher field respect to the signals of the homopolymer. The splitting is due to a change of the chemical environment produced when an itaconate unit is adjacent to a styrene one, and the shift to upper field is due to the OCH_3 or OCH_2 groups of itaconate are located inside of the protection cone of the styrene unit [21, 29]. The methyne carbon of the styrene unit (γ) also undergo splitting in two signals with a small shifting to higher field, indicating that this signal is also influenced by the itaconate units. The ^{13}C-NMR of DI-*16*-*co*-S exhibits a similar behavior to that described above for MeI-*n*-*co*-S, although in that case neither the shift nor splits are so noticeable

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[21]. The NMR results indicate without any doubt that the structure of these copolymers has mainly random structures. If the obtained products were alternating or block copolymers the splitting and the shifting of the signals would not be observed.

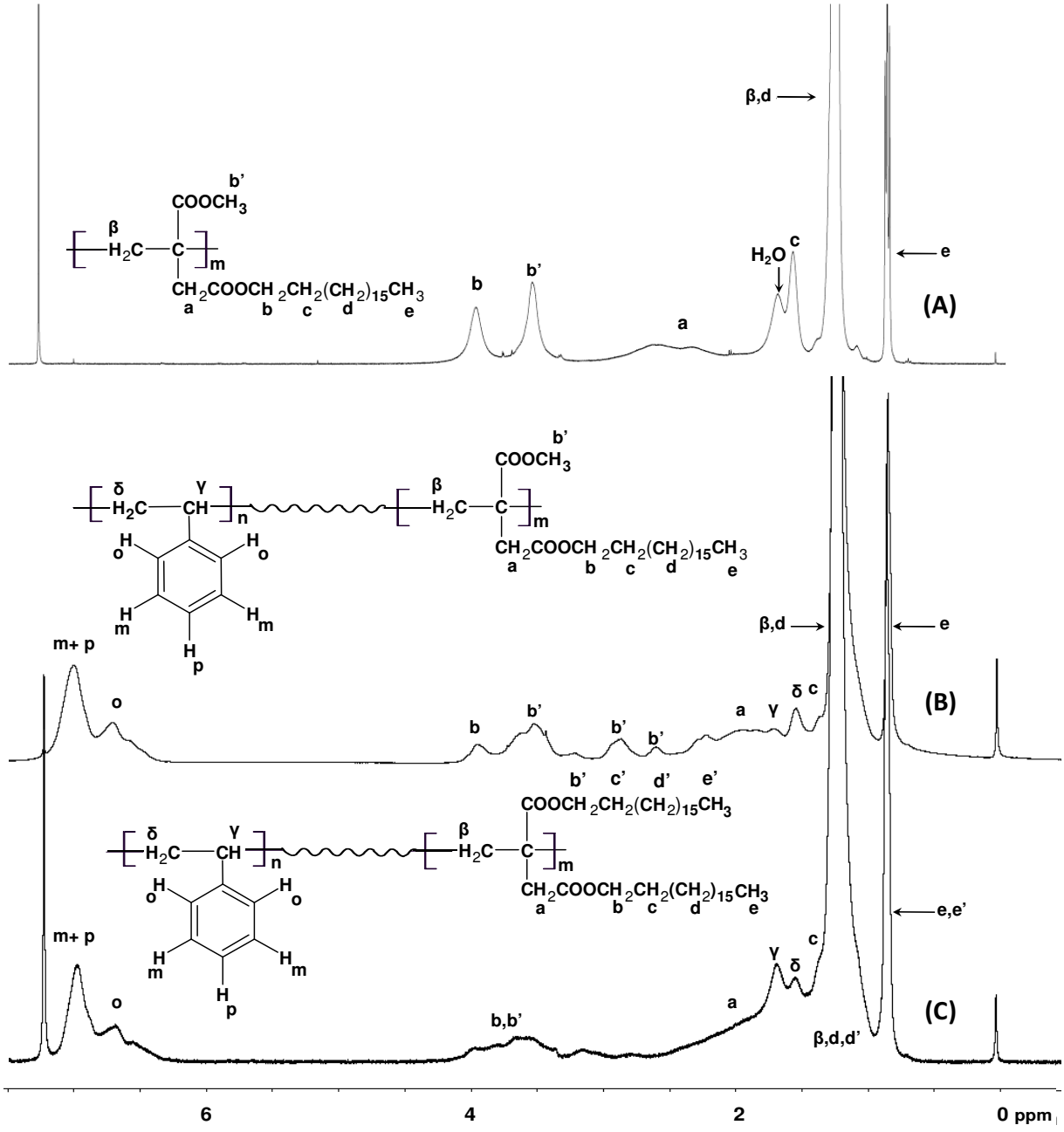


Figure 3. [1]H-NMR spectra in deuterated chloroform of PMeI-*18* (A), PMeI-*18*-*co*-S (1:1) (B), and PDI *18*-*co*-S (1:1) (C).

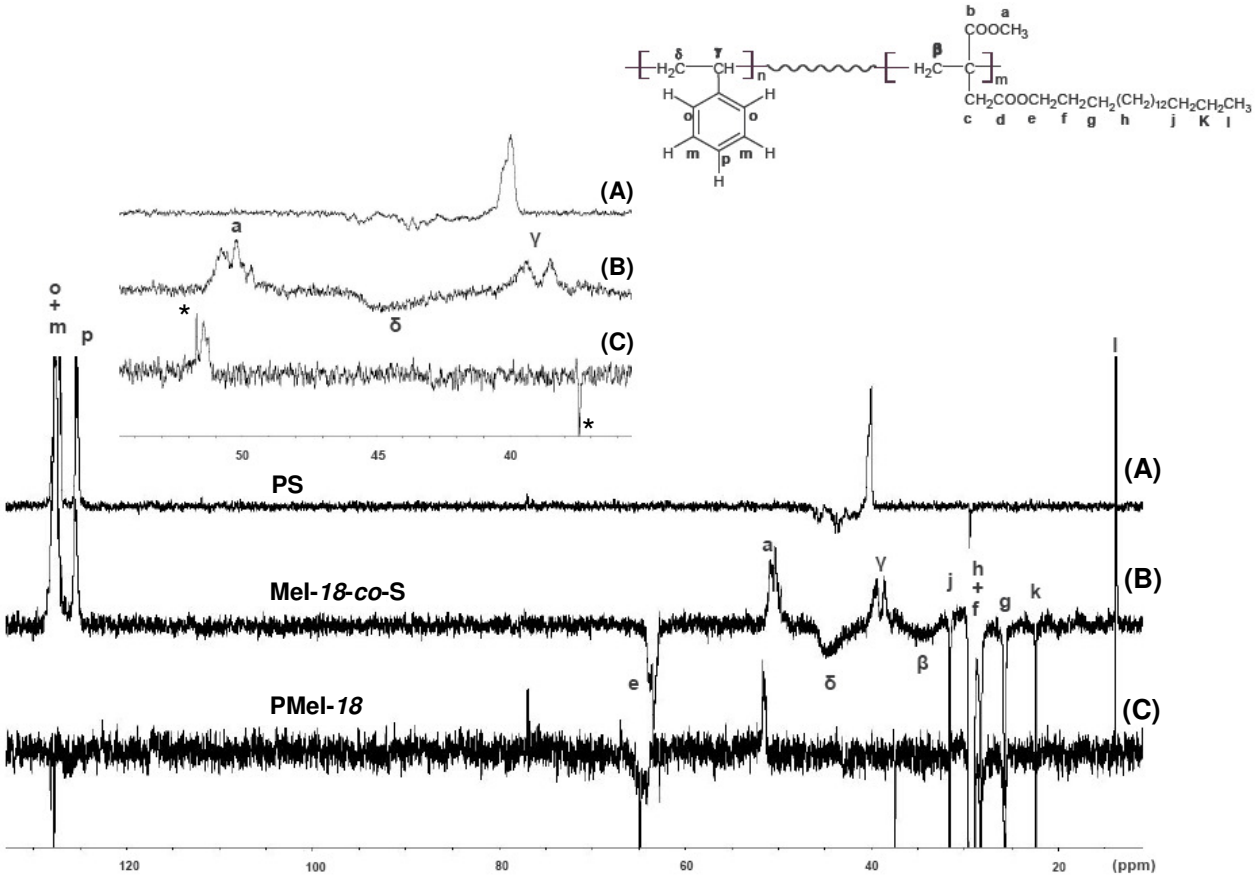


Figure 4. DEPT 135 in $CDCl_3$ of A) PS, B) MeI-*18*-*co*-S(1;1) and C) PMeI-*18*. The signals labeled with asterisk in C) are small remainder monomer in the homopolymer.

3.2 Reactivity ratios determination

The reactivity ratios were determined from the monomer proportion in the feed and the copolymers composition. As mentioned before, ^{1}H-NMR was used to quantify the copolymer composition and the FR, KT methods and a modification of the last one were used to determine the reactivity ratios. Reaction times of one hour allow to obtain yields of about 10% or less, which according to the previous report is necessary to apply in these methods [30, 31].

As an example in Figure 5 are shown the plots obtained for the calculated parameters for DI-*18*-*co*-S copolymers and in Table 3 the values of r_1 and r_2 for the whole series obtained by the three methods.

As it may be appreciated in Table 3, the obtained values for r_1 and r_2 for each one of the members of DI-*n*-*co*-S series were similar for the tree methods. Even more, in all cases is observed that r_1 and r_2 are less than unity and $0 < r_1 \cdot r_2 < 1$, indicating that this systems, as in many cases, generate random copolymers but with some tendency to alternation. In the case of the copolymers derivatives from DI-*12*, *14* and *16*, r_2 was slightly higher than r_1, indicating that styrene units are easier incorporated into the copolymer chain than those of itaconate. While the values for r_1 and r_2 in DI-*18* and *22* are closer but with r_1 slightly higher than r_2.

In the four series of MeI-*n*-*co*-S studied here, the values of r_2 were higher than r_1 regardless of the side chain of the itaconate and the difference between r_2 and r_1 for MeI-*n*-*co*-S with *n*=12, 14 and 16 was much more pronounced than in the previous cases.

These facts indicate that longest chains in the itaconate, 18 and 22, promote the incorporation of both monomers almost in the same form to the polymer chain, but the shorter ones promote the

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preferential incorporation of the styrene. This behavior is more pronounced in the MeI-*n* family as may see in Table 3. At the moment we do not have a satisfactory explanation to this behavior, since nor electronic or steric factor appear to be involved here. More studies must be carried out with others itaconates in order to obtain more conclusive results.

Equation (5) could be applied in most cases and the obtained values were similar to those observed with the FR or KT methods, as may be observed in Table 3. However, for the copolymers MeI-*12*-*co*-S and MeI-*14*-*co*-S, where there is a markedly difference between the values of r_1 and r_2, linearity was not observed when this equation is used. This indicates that this equation is only valid when the values of r_1 and r_2 are close and the intercept is small, since this treatment gives equal weight to the variables of the equation. If these values are very different, this treatment is no longer applicable.

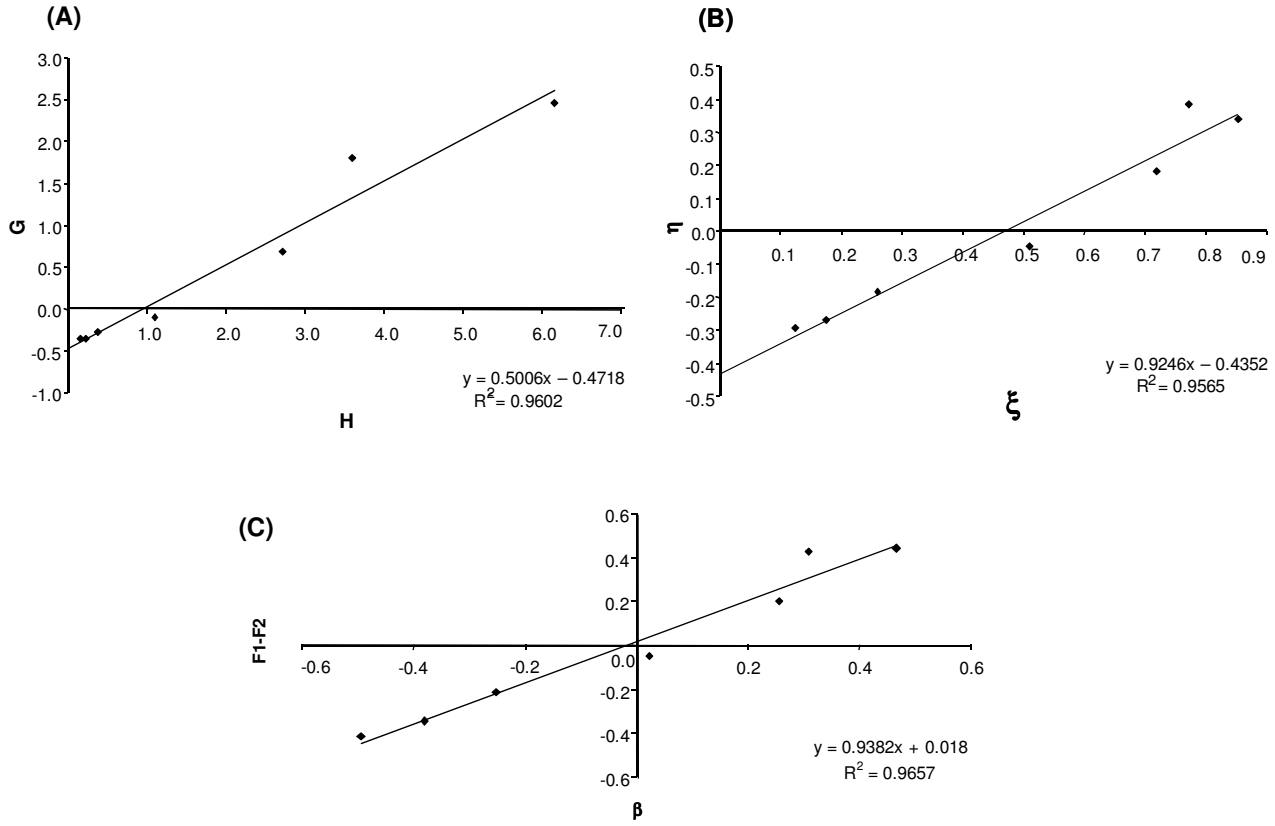


Figura 5. (A) FR (B) KT and (C) modified KT plots for DI-18-*co*-S.

Finally these results indicate that the monomeric units have some tendency to be distributed randomly in the copolymers, which is concordant with the NMR results. At this moment, we are carrying out further work in copolymerization of itaconates with styrene in order to reach more conclusive results related with copolymerization and the structure of these copolymers, and also to evaluate their thermal properties and the effect of styrene on the crystallization of *n*-alkyl side chains of itaconate.

4. CONCLUSIONS

Copolymerization of long side chain DI-*n* and MeI-*n* with S at low conversions provides random copolymers but with some tendency to alternation as was demonstrated by NMR, and confirmed by the methods used for the determination of the reactivity ratios.

In the case of the DI-*n*-*co*-S copolymers with *n* = 12, 14 and 16 the $r_{1(DI)}$ and $r_{2(S)}$ values were in the order de 0.2 to 0.3 being those of $r_{2(S)}$ greater than

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Table 3. Comparison of the values of reactivity ratios in the copolymerization between *n*-alkylitaconates and S obtained using the three methods.

	DI-*12*-*co*-S	DI-*14*-*co*-S	DI-*16*-*co*-S	DI-*18*-*co*-S	DI-*22*-*co*-S	MeI-*12*-*co*-S	MeI-*14*-*co*-S	MeI-*16*-*co*-S	MeI-*18*-*co*-S
Fineman-Ross									
r_1	0.22±0.03	0.19±0.02	0.25±0.04	0.50±0.05	0.46±0.03	0.02±0.01	0.10±0.02	0.38±0.06	0.42±0.03
r_2	0.28±0.12	0.18±0.08	0.35±0.16	0.47±0.13	0.44±0.10	0.97±0.07	0.54±0.13	0.84±0.16	0.44±0.10
R^2	0.93	0.96	0.90	0.96	0.97	0.93	0.84	0.94	0.98
Kelen Tüdös									
r_1	0.28±0.10	0.23±0.16	0.23±0.10	0.49±0.14	0.42±0.13	0.02±0.03	0.10±0.06	0.41±0.22	0.46±0.11
r_2	0.39±0.04	0.25±0.06	0.30±0.04	0.46±0.05	0.38±0.05	0.93±0.04	0.53±0.03	0.89±0.09	0.52±0.05
R^2	0.95	0.80	0.93	0.96	0.95	0.99	0.97	0.96	0.98
Modified Kelen Tüdös									
r_1	0.26±0.05	0.22±0.14	0.23±0.10	0.48±0.13	0.42±0.13	---	---	0.34±0.22	0.45±0.11
r_2	0.37±0.05	0.26±0.14	0.31±0.10	0.45±0.13	0.37±0.13	---	---	0.83±0.22	0.51±0.11
R^2	0.95	0.86	0.94	0.97	0.95	---	---	0.96	0.98
Average values using all methods									
r_1	0.25±0.17	0.21±0.11	0.24±0.08	0.49±0.11	0.43±0.10	0.02±0.02	0.10±0.04	0.38±0.17	0.44±0.08
r_2	0.35±0.18	0.23±0.09	0.32±0.10	0.46±0.10	0.40±0.09	0.96±0.05	0.54±0.08	0.85±0.16	0.49±0.09
$r_1.r_2$	0.09±0.10	0.05±0.04	0.08±0.05	0.22±0.10	0.17±0.08	0.02±0.02	0.05±0.03	0.32±0.20	0.22±0.08

$r_{1(DI)}$. These results could be interpreted as a slightly higher incorporation of styrene than itaconate in the copolymer. For the DI-*18* and *22*, the r values were between 0.4 and 0.5 and $r_{1(DI)}$ was slightly higher than $r_{2(S)}$ indicating in this case a slightly preferential incorporation of the itaconate in the copolymer. However, this interpretation should be taken with some caution since the values are close and the errors are not negligible. Therefore we consider that additional studies must be carried out to reach more conclusive results.

Although for MeI-n-*co*-S the tendencies were more or less the same observed for the diitaconate copolymers, the values of $r_{2(S)}$ were ever higher that $r_{1(DI)}$ and their differences increase as the itaconate *n*-alkyl side chain become shorter.

The modification of the KT method carried out in this work and resumed in the equation (5) for the determination of reactivity ratios, showed that it is only applicable when the values of r_1 and r_2 are too close. This method works satisfactorily when was used in all the DI-*n*-*co*-S series, but when was used in the copolymerization of MeI-*n* only works adequately when the monomers were MeI-*16* and MeI-*18*.

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